SPACE GRADE CHEMICALLY FOAMED SILICONE ELASTOMERS

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SUMMARY

Space grade chemically foamed elastomers are prepared by subjecting the foams prepared from conventional silicones to a thermal vacuum stripping exposure after the normal cure and postcure treatments. The resulting foams meet all the weight loss and volatile condensible materials criteria required for a space grade material. They are much more economical to prepare than would be the foams prepared from the space grade silicones as starting materials. They possess physical and thermal properties similar to or superior to those foams which have not been given the stripping treatment.

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1.0 INTRODUCTION

Chemically foamed silicone elastomers are available in a variety of densities and compositions and are widely used as insulation systems and/or insulators - ablators for various space and re-entry applications. The main advantages of the chemically foamed systems over the syntactically filled silicones are their lower modulus and higher elongations to failure. The resulting flexibility provides for ease of application of the foamed materials.

Normally, the chemically foamed materials are made in block form. The base Room Temperature Vulcanizing (RTV) silicone is blended with the foaming agent, the catalyst is then blended in and the mixture poured into a simple pan-type mold, where it is allowed to foam and cure at room temperature. The top skin is removed and the block is then subjected to the normal cure and post cure cycle. This is then slit on a conventional rubber slitting machine to the desired thickness. Normally, blocks measuring 30" x 30" are made in thicknesses ranging up to 6 or more inches. Sheets may then be skived at thicknesses ranging from a minimum of approximately 0.080" (depending on the density) to a maximum of 6" or more.

The flexibility of the sheets permits their application to many surfaces by a technique similar to that used in "wallpapering". In all cases, the surfaces must be cleaned thoroughly, degreased and primed with a silicone primer. After proper cure of the primer, the adhesive which is the unfoamed, base RTV silicone is applied to the surface. Normally, thicknesses of 10-15 mils of the adhesive are applied, and usually with a hard rubber roller, although it may be applied by spraying or by brushing. Then the sheets are applied and held in place with slight pressure, until the adhesive cures.

In addition to sheet stock applications, the material can be spray applied in thicknesses ranging from 3 - 5 mils up to 0.4". For complicated and/or inaccessible areas, molded-to-shape parts can be made and applied by adhesive bonding.

Although, as is shown later, the foamed silicones are excellent insulators, one of their main disadvantages arises from the fact that the silicones as normally prepared and cured, contain as much as 4 - 6% by wt. of volatile components, which will outgas in the low pressures encountered in space. In addition, the volatiles components may condense on colder or more polar surfaces, and cause undesirable fogging of windows, or undesirable contamination of other components.

2.0 VARIETIES OF FOAMED SILICONE ELASTOMERS

There are two distinct families of the foamed silicone elastomers. One was developed as an ablator/insulator material for lifting entry type applications. These are called the Elastomeric Shield Materials (ESM) and contain short length inorganic fibers to promote the formation of a hard char and to enhance char retention by the virgin material. Several types of ESM are currently in use. Some of these are fabricated in a honeycomb support for improved shear resistance capability. Table 1, lists the common ESM materials along with their densities and descriptions.

The members of the other family of foamed elastomers do not contain the inorganic fibers and are used essentially as insulations. These are designated PD 200 and are made in two different varieties, as shown in Table 2.

Table 1

TYPES OF ESM FOAMED SILICONE ELASTOMERS

Material	Density (p.c.f.)	Description
ESM 1004 X	16	Unsupported
ESM 1004 X (NS)	22	Nomex honeycomb support
ESM 1004 AP	34	Unsupported
ESM 1001 P(S)	42	Phenolic glass honeycomb support
ESM 1004 LP	50	Unsupported
ESM 1004 LP(S)	55	Phenolic glass honeycomb support

Table 2

TYPES OF PD200 FOAMED SILICONE ELASTOMERS

Material	Density (p.c.f.)
PD 200-16	16
PD 200-32	32

These may also be foamed in honeycomb supports if additional shear resistance is required. The absence of the inorganic fibers leads to lower moduli and higher elongations to failure. They are fabricated in the same manner as the ESM foams but the process is simplified since there is no requirement for milling the inorganic fibers into the base RTV silicone.

3.0 REDUCTION OF VOLATILE MATERIALS

There are two approaches for preparing silicone elastomeric foams which meet the requirements of a space grade material.

1. Use special, space-grade RTV silicones as starting materials. Both General Electric and Dow Chemical market space grade RTV silicones. However, such materials are very expensive (\$395.00 / lb) when compared with the regular grades, and besides could become contaminated during processing.

2. Another approach is to prepare the foams from the normal starting materials, and after the normal cure and post cure treatments, to subject them to a thermal-vacuum stripping treatment. This latter procedure has been adopted for both the ESM and PD200 families of materials in the sheet stock form. Naturally, the lower the pressure, the higher the temperature, and the longer the time of treatment the cleaner will be the resulting foams. However, temperatures should be kept at below $400^{o}F$ for extended exposures of 24 hours or more. In practice a temperature of $350^{o}F$ for 48 hours at pressures of 10^{-6} torr or lower have been found to be effective.

4.0 VOLATILE DETERMINATIONS

Weight loss and volatile condensible measurements have been made on the materials that had been subjected to the normal cure as well as those that were vacuum stripped. Measurements have been made both for ESM and PD200 that had received both treatments. The measurements were made at 10^{-6} to 10^{-8} torr, and $250^{o}F$ for twenty four hours. Samples were run by NASA-Goddard, Greenbelt, Maryland and by Ball Brothers Research Corporation (BBRC) Boulder, Colorado. The results of the determinations are summarized in Table 3.

Table 3

WEIGHT LOSS AND VOLATILE CONDENSIBLE MATERIAL DETERMINATIONS ON FOAMED SILICONE ELASTOMERS

Material	Treatment	Wt. Loss (%)	V.C.M. (%)	Determinations Made By
PD200-16	Normal cure & post cure	1.127	0.491	NASA-Goddard
PD200-16	Above & vacuum strip	0.033	0.025	NASA-Goddard
ESM1004X	Normal cure & post cure	4.26	1.12	NASA-Goddard
ESM1004X	Above & vacuum strip	0.17	0.0	NASA-Goddard
ESM1004AP	Normal cure & post cure	1.93	-----	BBRC
ESM1004AP	Above & vacuum strip	0.30	-----	BBRC
ESM1004LPS	Normal cure & post cure	1.41	-----	BBRC
ESM1004LPS	Above & vacuum strip	0.355	-----	BBRC

B.B.R.C. were not asked to determine the volatile condensible materials content. However, based on the experience with the NASA determinations it is safe to assume that the VCM content would be at least 0.1% for the non-stripped materials and would be less than 0.1% for the vacuum stripped materials.

It is evident that the vacuum stripping procedure provides material that meets the requirements for a space-grade material. Heated vacuum chambers have been used which permitted the simultaneous treatment of several blocks of material each 30" x 30" x 4" thick. Consequently, the large scale production of space grade material can be achieved.

The magnitude of the economies that can be realized by using the vacuum stripping procedure can be seen from a comparison of the raw material costs. The cost per pound for the space grade RTV silicone is $395.00 while the cost of the conventional material is not over $10.00 per pound. Since a large amount of foamed material can be treated in large, heated space simulators, the treatment costs per pound of material is of the order of $2 - $3 (for large batches of material). In addition, tests show very little difference in properties or behavior between the space grade foams prepared from conventional. Actually, as will be seen later the thermal conductivity and the ablation performance are both slightly improved as a result of the stripping procedure.

5.0 EFFECT OF VACUUM STRIPPING ON THERMAL & MECHANICAL PROPERTIES

5.1 Thermal Properties

Thermal conductivity, specific heat and TGA data have been obtained on various foams both in the virgin and in the vacuum stripped states.

1. Thermal Conductivity: Thermal conductivity measurements were made by the guarded hot plate both at atmospheric and at reduced pressures and at various temperatures. The results of typical measurements are illustrated in Figure 1 for ESM 1004AP. It is seen that in general, the thermal conductivity is highly dependent on the stripping treatment, being as much as 25% lower at $150^{\circ}F$ for the stripped material than for the non-stripped material. Hence, there is an immense thermal insulation advantage in using the stripping process.

2. Specific Heat: The specific heats were measured by Differential Scanning Calorimetry. The data are plotted as specific heat for each material - in both conditions. It is seen from Figure 2 the data for a given material (ESM1004LP) is the same whether it has been vacuum stripped or not.

3. Thermogravimetric Analyses (TGA) Characterization: Samples of both types of material were run in duplicate in 1 atm. nitrogen, 1 atm air, and at a pressure of 10^{-4} atm. in air. The results of the measurements for a typical material in both states are shown in Figure 3 & 4 as plots of residual weight fraction as a function of temperature.

FIGURE 1

THERMAL CONDUCTIVITY OF ESM 1004 AP

(1ATM. PRESSURE)

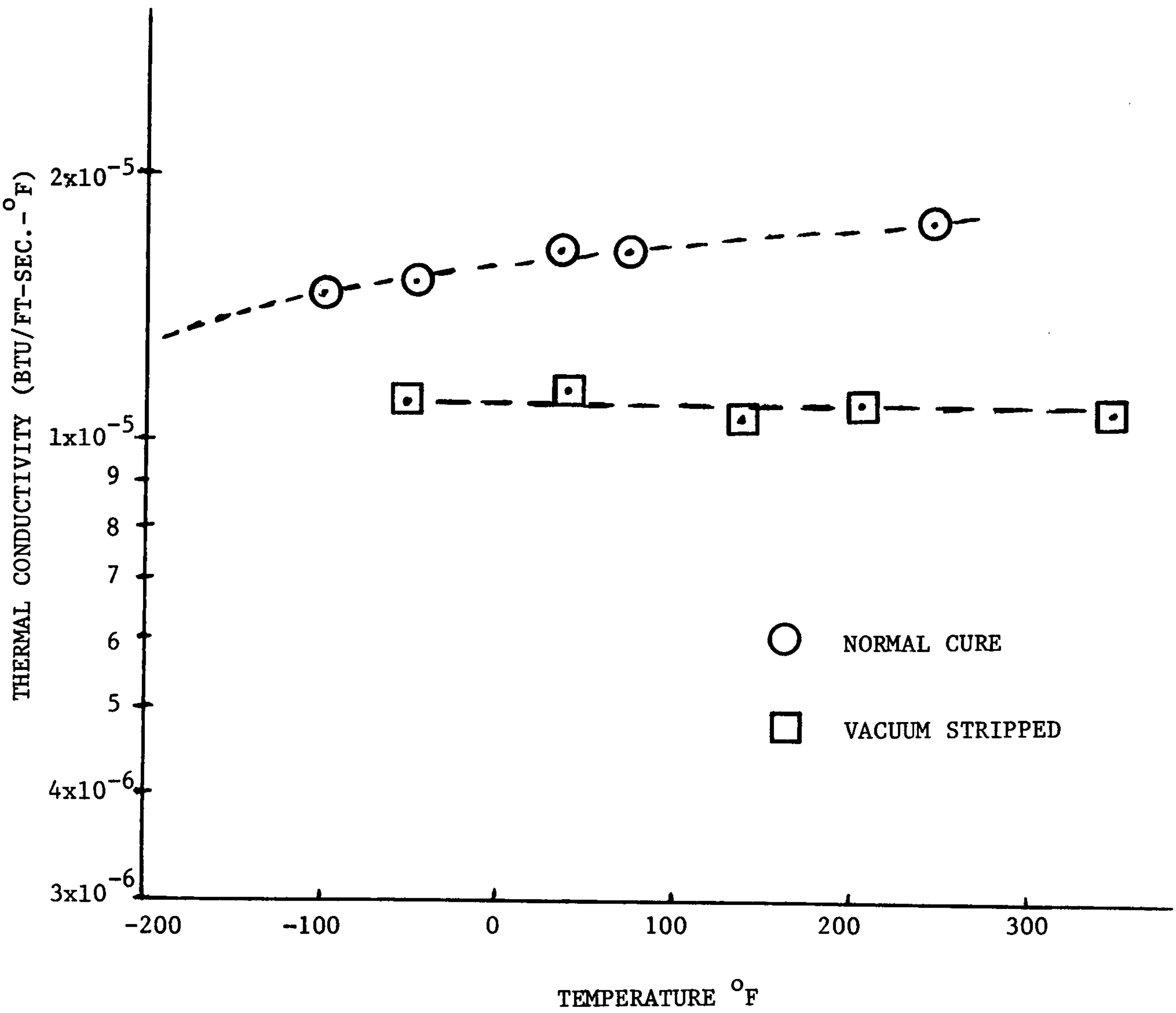


FIGURE 2

ESM 1004 LP SPECIFIC HEAT

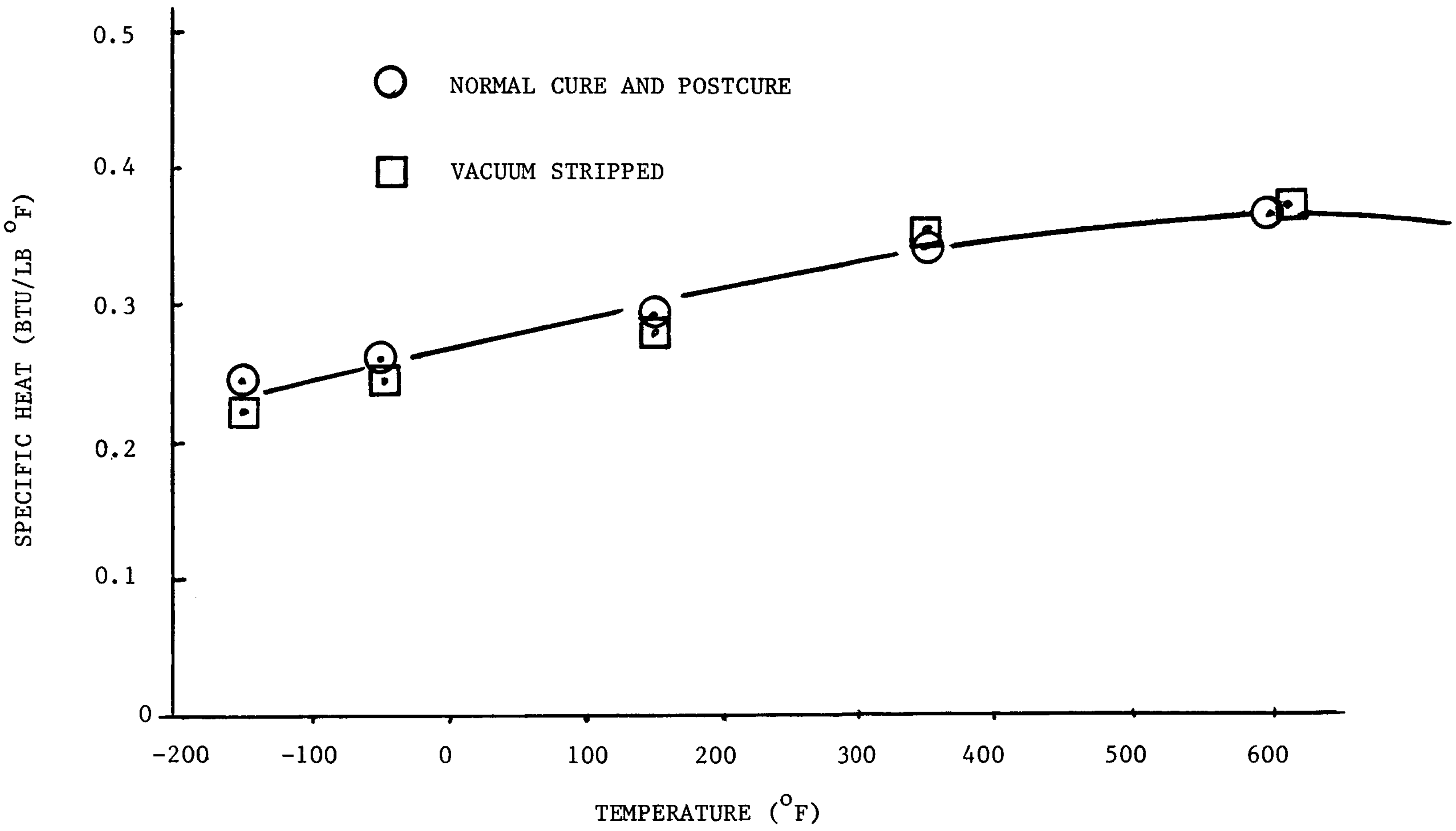


FIGURE 3

TGA OF ESM 1004 AP

NORMAL CURE AND POST CURE

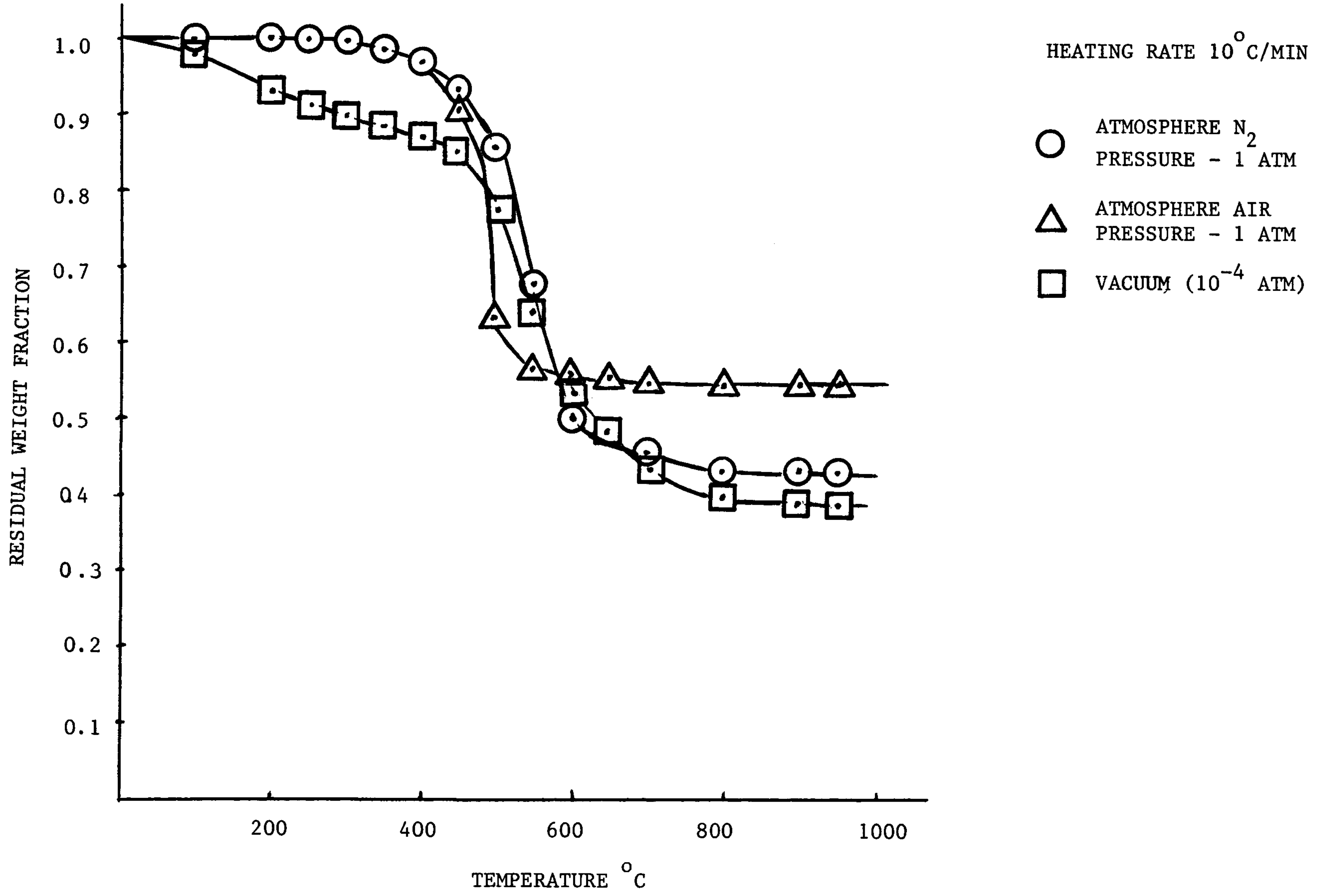
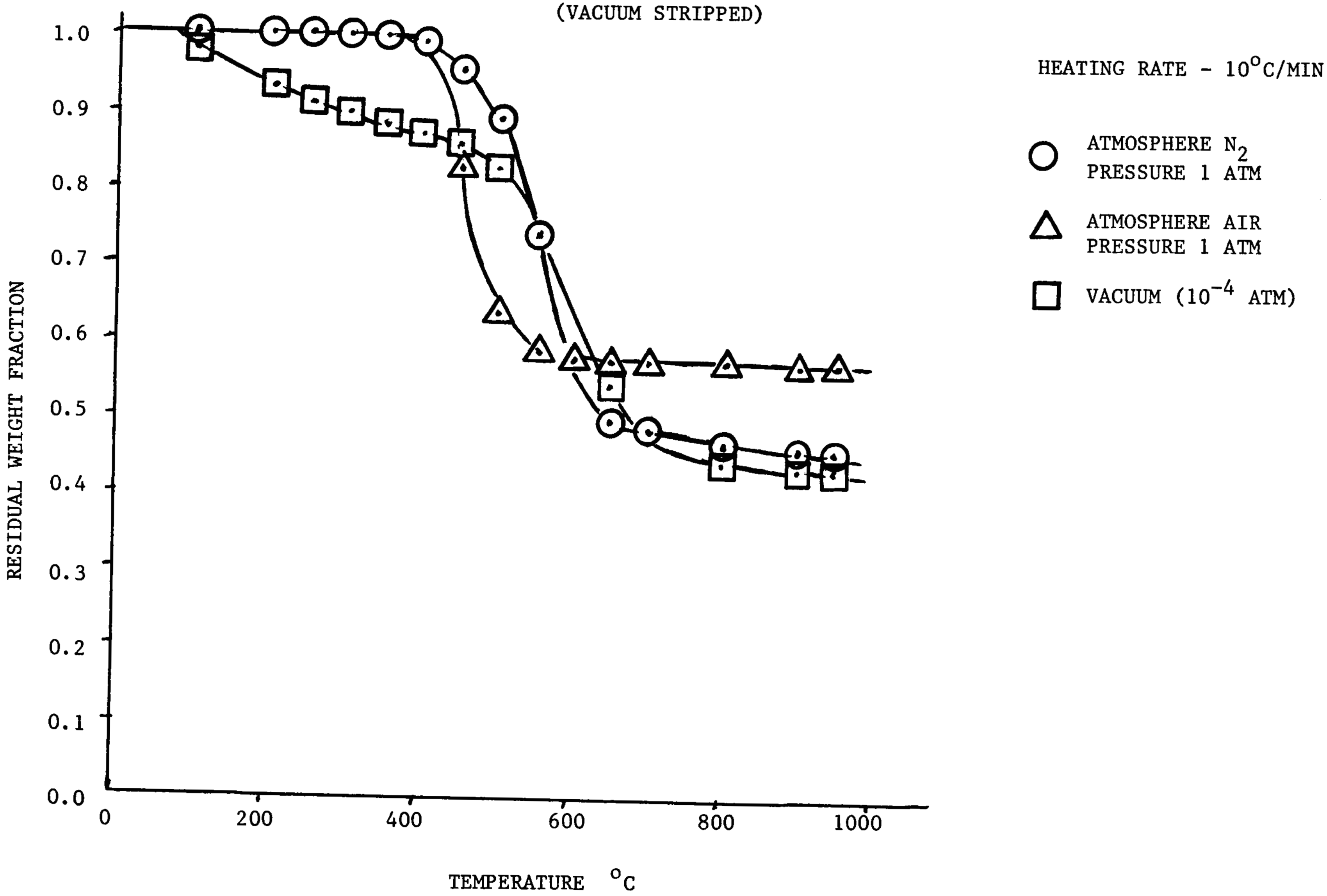


FIGURE 4

TGA OF ESM 1004 AP

(VACUUM STRIPPED)



In this analysis, the residual weight fraction at 900°C is used as a basis for comparison. Duplicate runs on the same material are all well within 2% with deviations of from 4-6% on specimens of the same type but from different lots. Greater initial weight losses were experienced in the order vacuum $>$ nitrogen $>$ air. The reason for the lower weight loss experienced in the degradation in air is the formation of non-volatile oxidation products.

The vacuum stripped specimens generally show slightly lower weight loss (ranging from 6 - 20%) than the virgin materials.

5.2 Physical Properties

In all cases, property measurements were made on the materials in two conditions, viz. virgin-as normally fabricated, and vacuum stripped.

Tensile, compression and thermal expansion data were obtained. Test specimen configurations and facilities use to obtain the data are summarized in Table 4 . All of the test techniques are considered as being standardized procedures and/or long standing use within GE/RESD.

1. Tensile Properties: The tensile property data are shown as functions of temperature in Figures 5, 6 and 7. The materials exhibited typical silicone behavior, i.e., a strong dependence of property on temperature including a two order of magnitude increase in modulus below the glass transition temperature.

2. Compressive Properties: Compressive secant modulus data are shown in Figure 8. The results show a slight increase in modulus with increasing temperature from 75°F to 600°F, which is typical silicone behavior. The vacuum stripping treatment appears to increase the stiffness of the silicone foams to a slight extent.

TABLE 4

ESM MECHANICAL PROPERTY CHARACTERIZATION TEST TECHNIQUES

TYPE OF TEST	PROPERTIES DETERMINED	TEST SPECIMEN GEOMETRY	TEST TECHNIQUE	TEST FACILITY
Tension	1. Ultimate Strength 2. Failure Strain 3. Initial Tangent Modulus (1) E 4. Poisson's Ratio (1)	"Dogbone" Tensile bar, ½ inch thick, 6 inches long, one inch wide reduced gage width.	Standard Tensile pull using pneumatic grips and two modified Instron strain gage extensometers to sense and record axial and transverse strains simultaneously	Instron Test Machine with environmental chamber: XYY recorder
Compression	Secant modulus at 5.0 percent strain	Rectangular parallelopiped (1 x 1 x 3 inches) loaded parallel to 3 inch direction.	Direction compressed between parallel platens in test machine; strain measured by crosshead displacement	Instron Test Machine with environmental chamber
Bond Shear	Mode of Failure (2) and shear stress at failure	Right circular cylinder, 3.0 in. O.D., 2.0 in. I.D., of ESM system/substrate bonded between two 3.0 in. O.D. Aluminum loading blocks.	Torsion of right circular cylinder about its axis	GE-RESD Torsion Test Machine with Environmental Chamber, XYY Recorder
Bond Flatwise Tension	Mode of Failure (2) and tensile stress at failure	One inch square ESM system/substrate bonded between aluminum loading blocks.	Tensile pull using Pin loading with clevice grips	Instron Test Machine with Environmental Chamber
Thermal Expansion	Thermal Strain vs. Temperature, $\Delta L/L_o$ vs. T	3/4 x 3/4 x 2.00 inches	Quartz Tube Dilatometry with continuous ΔL vs. T measurement using LVDT	GE-RESD low temperature dilatometer system

NOTES:

(1) E and μ to be determined by three non-destructive loadings of each specimen

(2) ESM anticipated to fail at lower stress than bond

FIGURE 5

TENSILE STRENGTH OF ESM 1004-AP

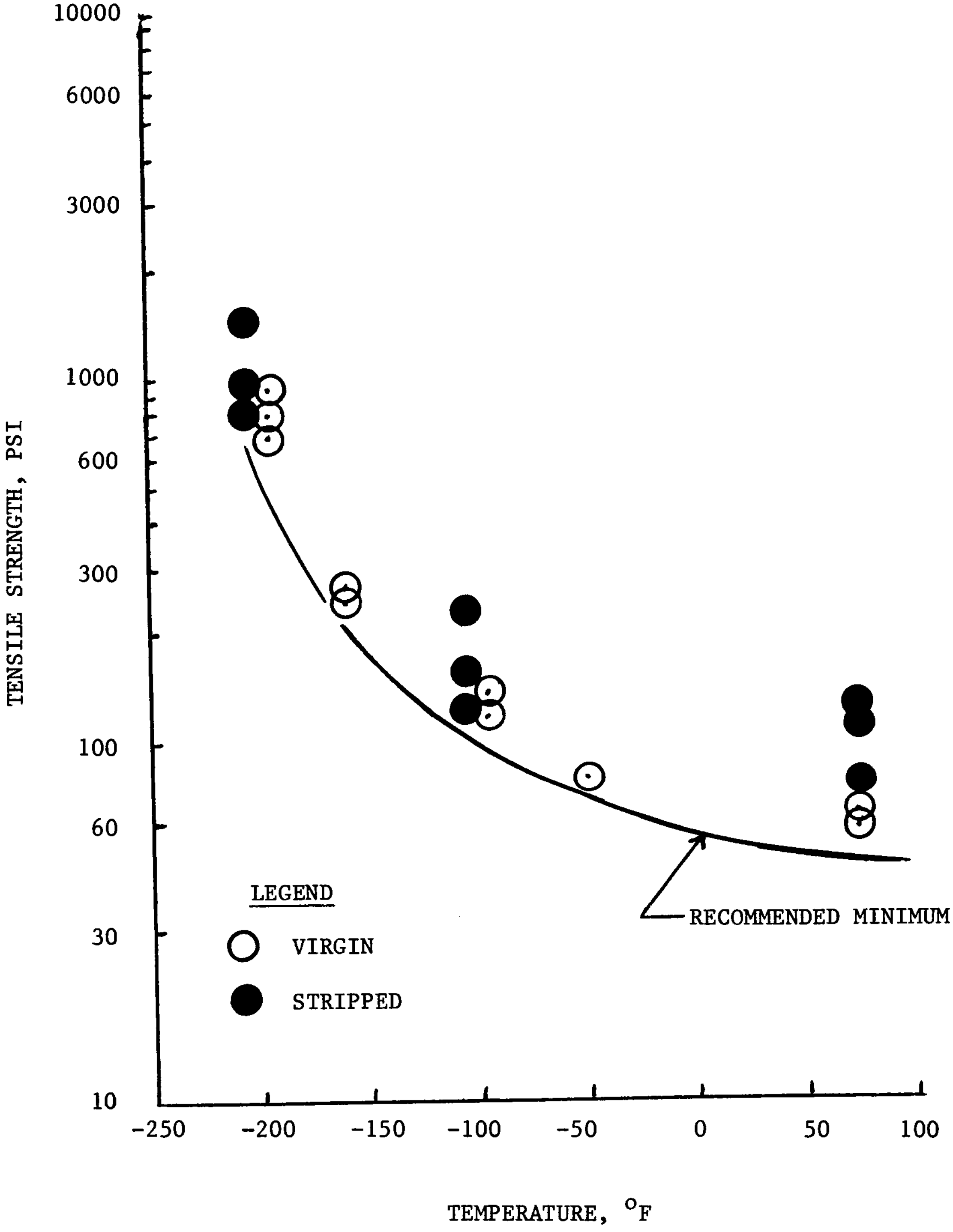


FIGURE 6

TENSILE MODULUS OF ESM 1004-AP

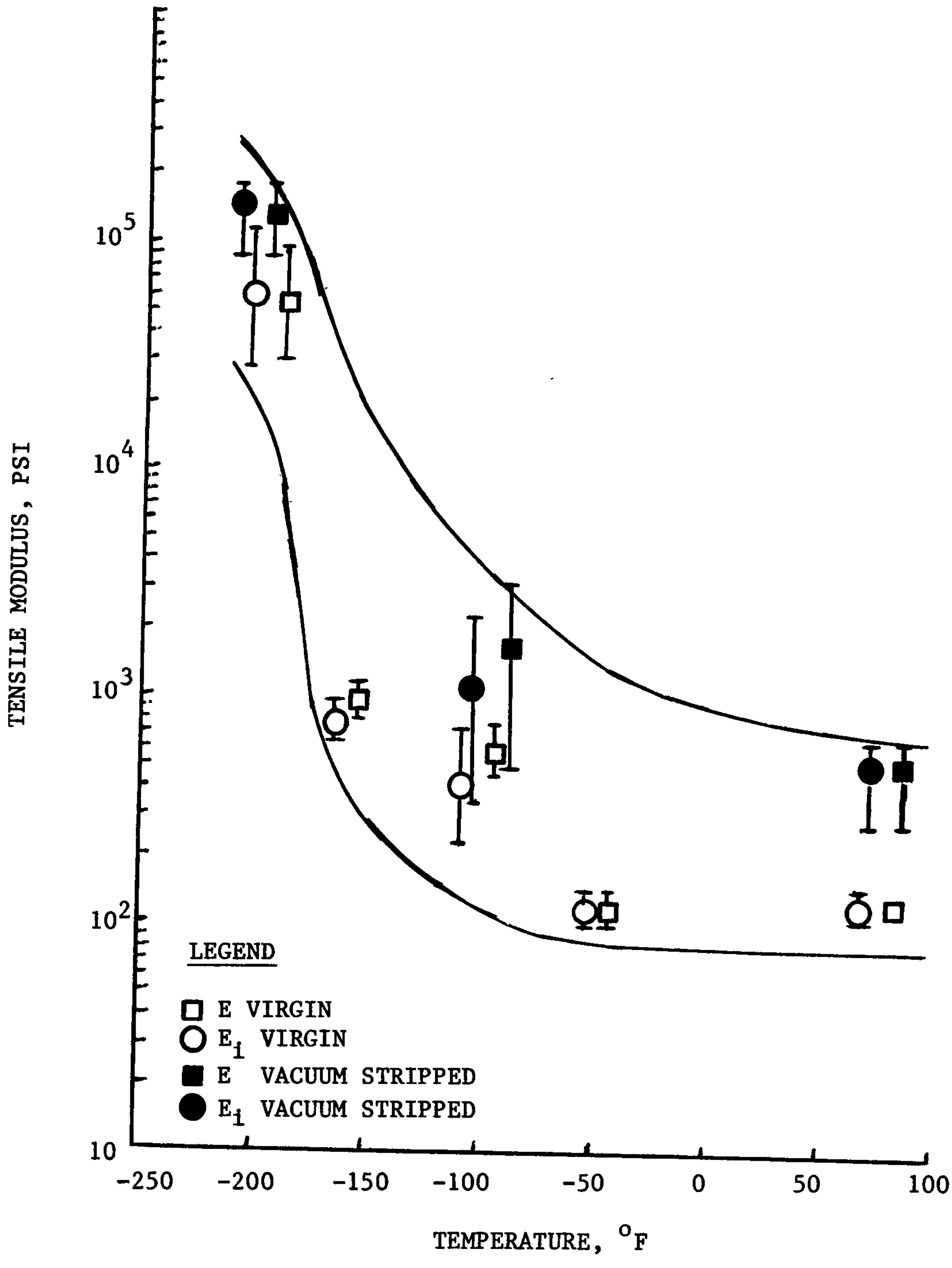


FIGURE 7

FAILURE STRAIN OF ESM 1004-AP

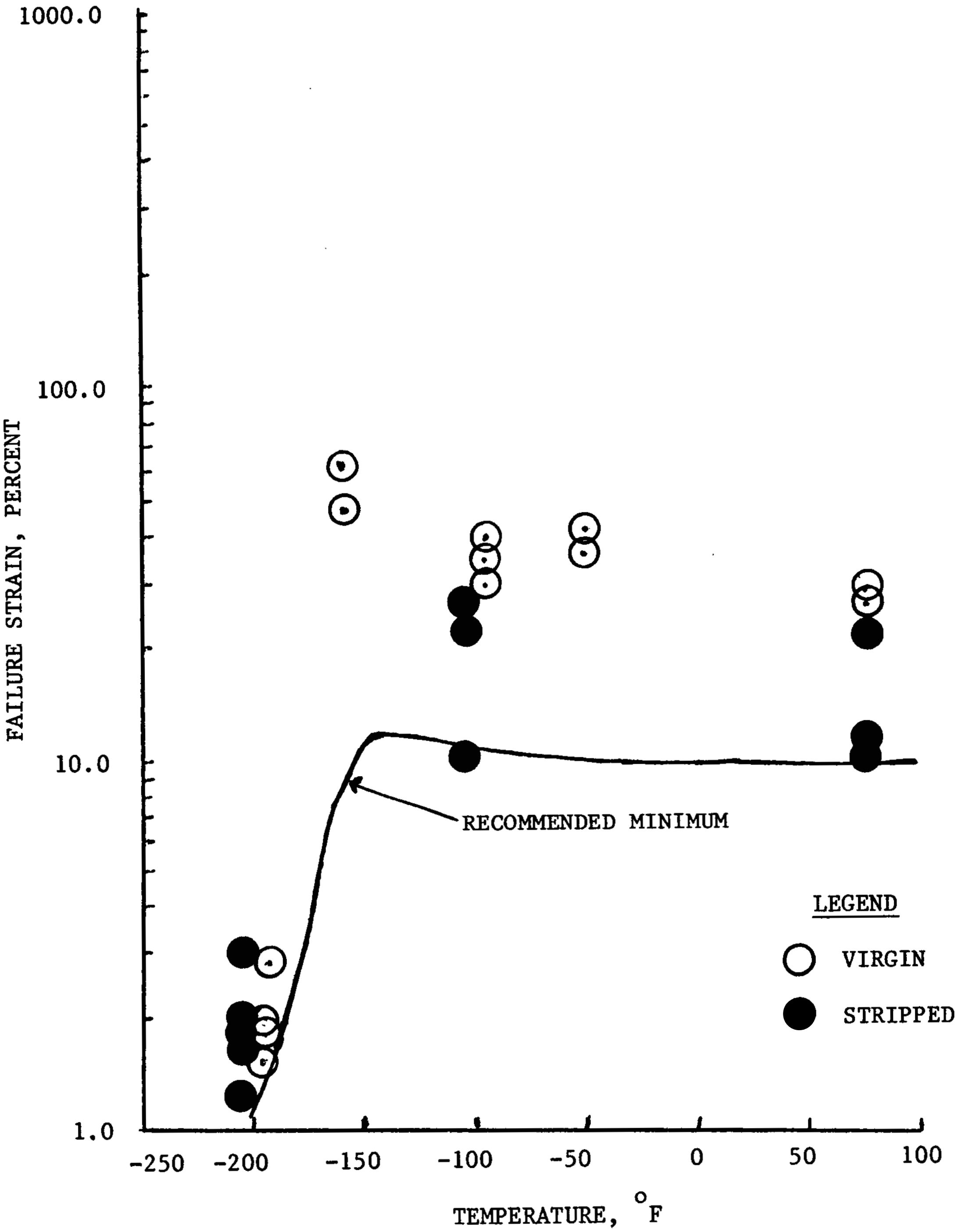
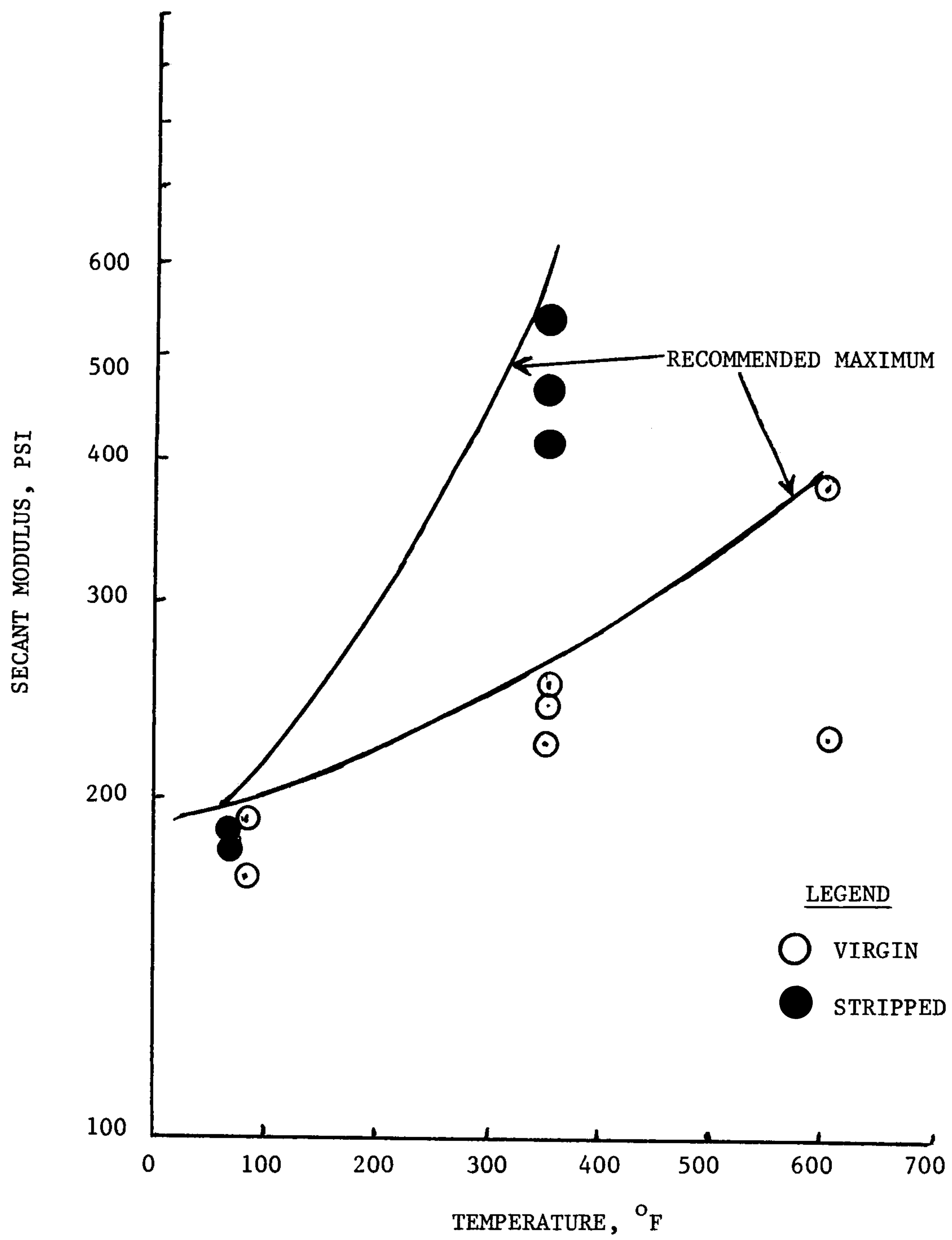


FIGURE 8

COMPRESSIVE SECANT MODULUS OF ESM 1004-AP



3. Thermal Expansion Properties: Results of thermal expansion measurements and recorded in Figures 9 and 10 as plots of Δ L/L as a function of temperature. Figure 11, which is included for reference, shows the thermal expansion behavior of the base RTV silicone. In general, the foamed silicones exhibit the typical silicone behavior: a high coefficient of expansion above the glass transition temperature and a significantly lower coefficient below. The transition occurs over a temperature range, which is normal, but is generally completed at around $-175^{o}F$ for materials based on this particular type of RTV silicone rubber.

The vacuum stripping treatment appears to have little or no effect on the thermal expansion behavior.

5.3 Bond Shear Tests

The bond shear test results are given in Table 5. Tests were also made on honeycomb supported material and it is seen that all these specimens (ESM1004LPS) exhibited cohesive failure in the RTV silicone bond line. This indicates that the full shear capability was developed and demonstrates the adequacy of the adhesive in a shear stress condition.

5.4 Bond Flatwise Tensile Tests

The adequacy of the adhesive bond was also evaluated by flatwise tensile testing. A sketch of the test specimen and a listing of its possible failure modes are given in Figure 12. Of these potential failure modes, only code "D", adhesive, RTV silicone/phenolic glass is indicative of a poor bond. Modes of failure "E" and "F" reflect problems associated with specimen preparation while modes of failure "A", "B", and "C" are all acceptable from the system standpoint.

FIGURE 9

THERMAL EXPANSION OF ESM 1004-AP

(VIRGIN MATERIAL)

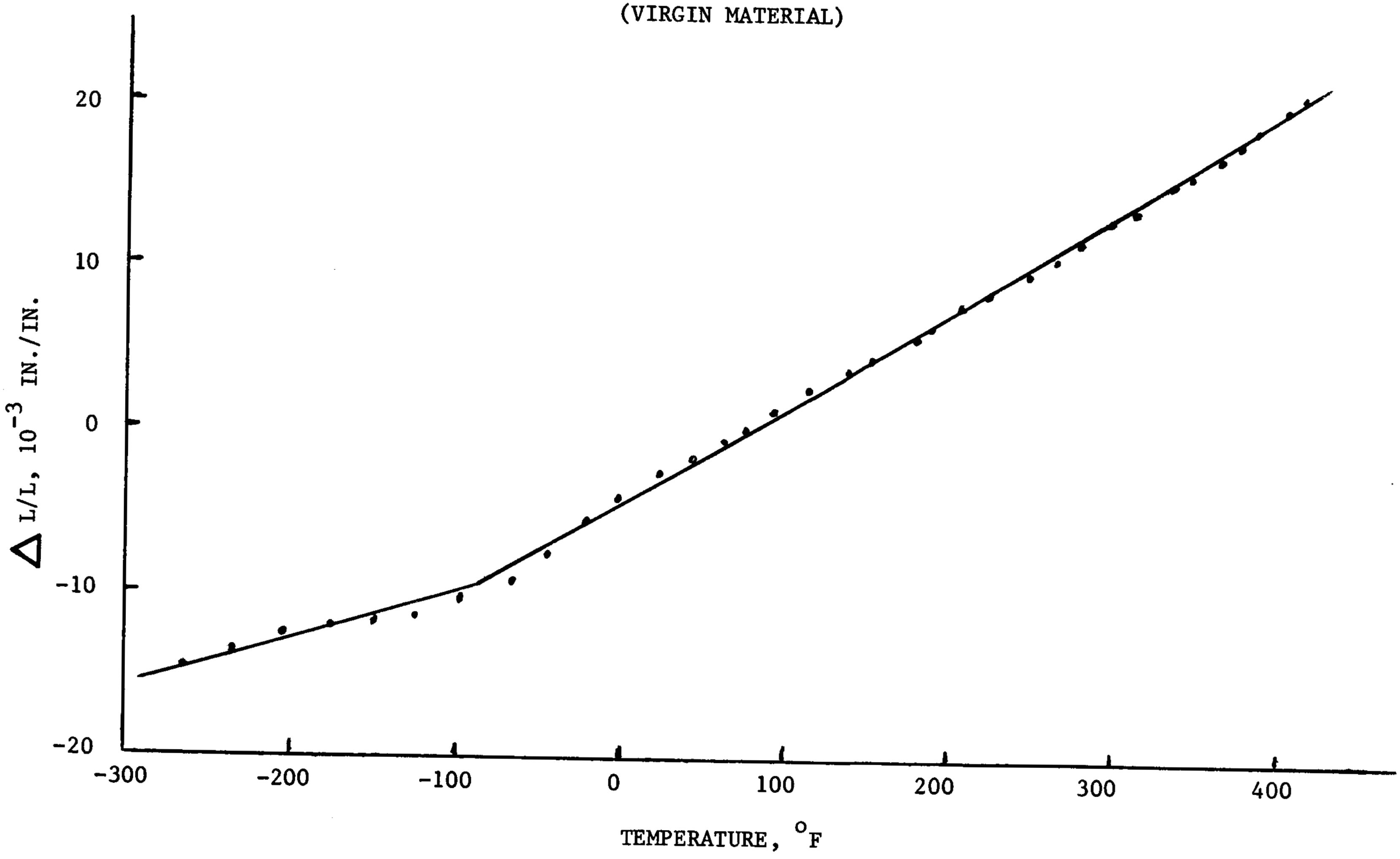


FIGURE 10

THERMAL EXPANSION OF ESM 1004-AP

(STRIPPED)

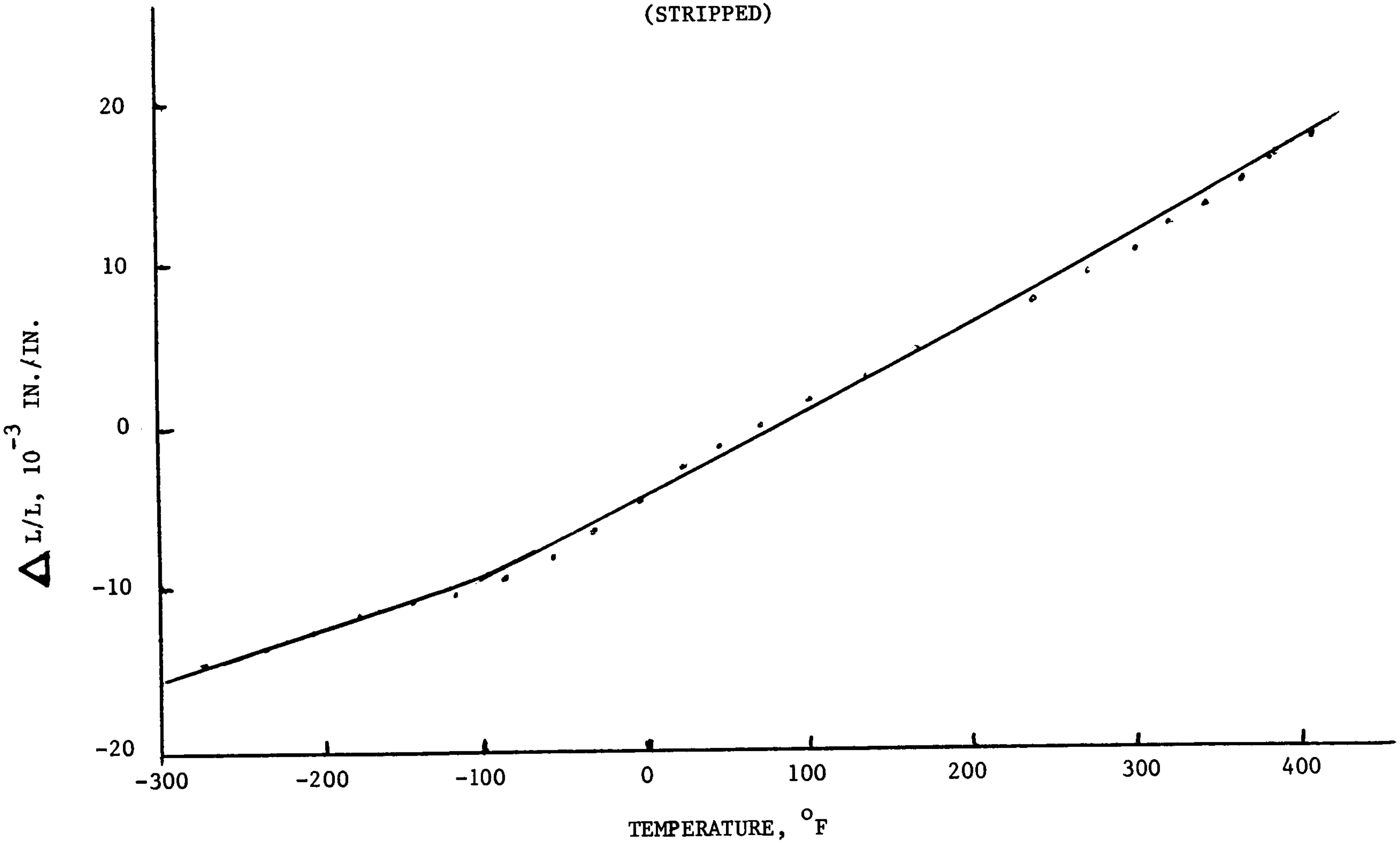


FIGURE 11

THERMAL EXPANSION OF RTV-560

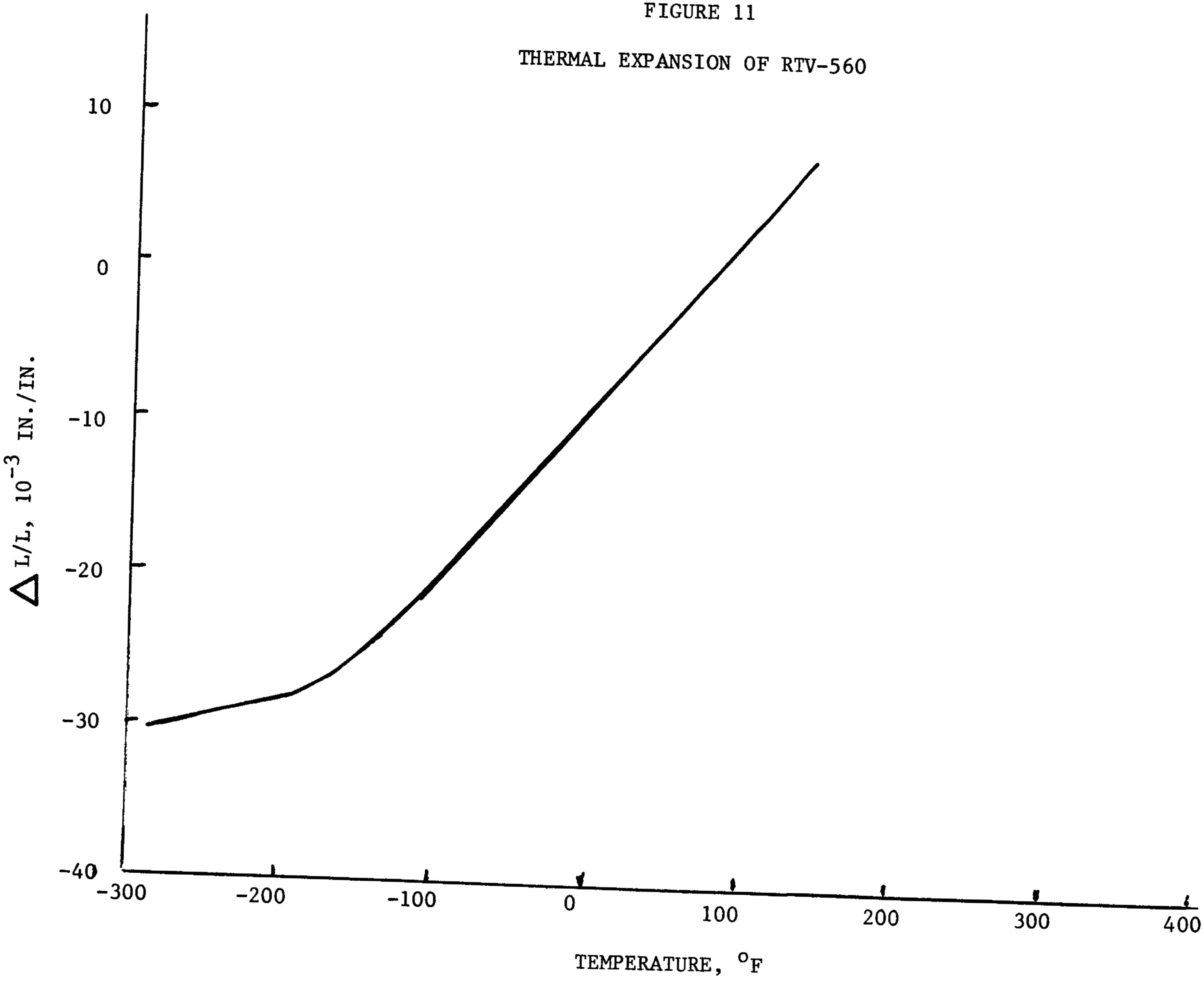


TABLE 5

BOND SHEAR (TORSION) TEST RESULTS

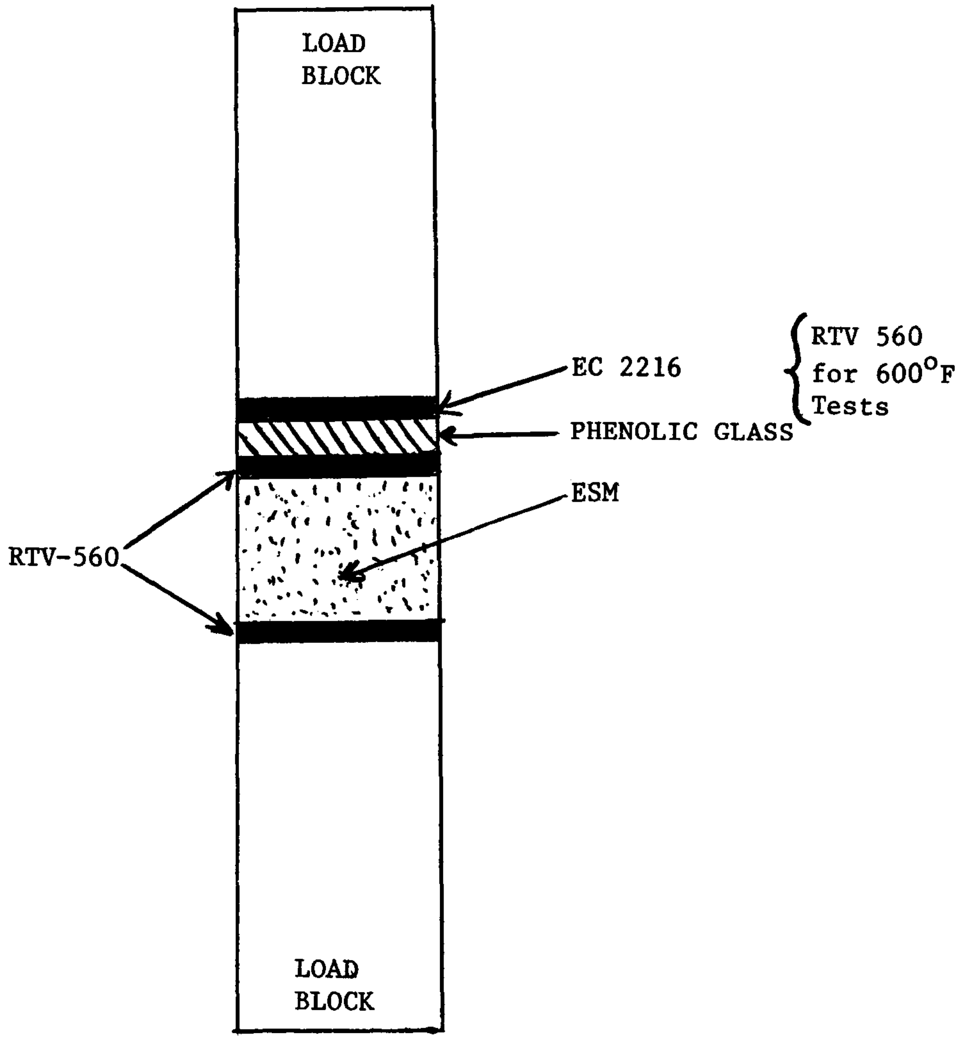
Temperature = 350°F

MATERIAL	SPECIMEN NUMBER	SHEAR STRENGTH (psi)	MODE OF FAILURE* A	B	C	D
	V-L-S-1-H	-				100
ESM 1004-LP	-2	41.1			100	
(Virgin)	-3	16.4			100	
	-4	17.6			100	
	-5	25.4			100	
	V-PS-S-1-BB	105	100			
	-2	111	100			
ESM 1004-LPS	-3	118	100			
(Virgin)	-4	112	100			
	-5	111	100			
	$\bar{X}$	112				
ESM 1004-LPS	P-PS-S-1-EE	141	100			
(Pre-conditioned)	-2	54	50	50		
	-3	131	100			

* A: Cohesive in RTV-560 Bond
B: Adhesive to Aluminum
C: Adhesive to Phenolic Glass
D: Damaged in Processing

FIGURE 12

POSSIBLE FAILURE LOCATIONS FOR BOND FLATWISE TENSION TESTS



MODES OF FAILURE:

A. COHESIVE IN ESM
B. COHESIVE IN PHENOLIC GLASS
C. COHESIVE IN RTV-560
D. ADHESIVE RTV-560/PHENOLIC GLASS
E. ADHESIVE RTV-560/ALUMINUM

The bond flatwise tensile data are recorded in Tables 6 and 7. They are all considered to be acceptable, thus once again establishing the adequacy of the base RTV silicone bond.

A comparison of the strength values obtained for ESM 1004AP in these tests with the dogbone tensile data reveals generally good agreement, although the flatwise tensile strengths tend to be slightly lower. This is probably due to the presence of a small but significant degree of anisotropy which results from the foaming operation.

5.5 Thermostructural Capability

Panels of various foamed silicones measuring 12" x 12" x 1" thick were bonded with the base RTV silicone to panels of aluminum, titanium, stainless steel, and fiberglass. These were cycled over the temperature range of $-300^{o}F$ to $+600^{o}F$ at heating and cooling rates of $3^{o}F$/minute without failure.

5.6 Ground Ablation Tests

Numerous tests have been run under various heating conditions in the G.E. 5MW hyperthermal arc facility on the normal ESM formulations. In addition, several tests were recently run on the stripped material. Typical data are shown in Figure for the ESM 1004AP. In general, the stripping procedure significantly reduces the magnitude of recession due to ablation. No adverse effects of the stripping procedure were noted in any of the ablation tests.

6.0 ACKNOWLEDGEMENTS

The author gratefully acknowledges the assistance of all those who made the various measurements and who conducted the tests described in this paper. The process described in the paper was developed under General Electric funding.

TABLE 6

ESM 1004-AP BUTT TENSION TEST RESULTS
(VIRGIN MATERIAL)

SPECIMEN NUMBER	TEST TEMPERATURE (^{o}F)	FAILURE STRESS (psi)	MODE OF FAILURE (PERCENT) A	B	C
V-A-F-11-Z		995	100		
-12		844		100	
-13	-200	903	100		
-14		1031	90	10	
-15		994	100		
$\overline{X}$		953			
V-A-F-6-Z		122.4	100		
-7		83.8	100		
-8	-100	110.1	100		
-9		104.0	100		
-10		106.5	100		
$\overline{X}$		105.4			
V-A-F-1-Z		61.0	100		
-2		62.8	100		
-3	75	69.6	100		
-4		69.0	100		
-5		66.7	100		
$\overline{X}$		65.8			
V-A-F-16-Z		52.3	100		
-17		45.5	100		
-18	350	44.1	100		
-19		53.5	100		
$\overline{X}$		48.8			
V-A-F-1-S		17.7	100		
-2		19.1	100		
-3	600	13.9	100		
-4		11.2	15		85
-5		19.1	100		
$\overline{X}$		16.2			

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TABLE 7

ESM 1004 AP BUTT TENSION TEST RESULTS
(PRECONDITIONED MATERIAL)

SPECIMEN NUMBER	TEST TEMPERATURE (^{o}F)	FAILURE STRESS (psi)
P-A-F-1-S		805
-2	-200	802
-3		490
$\overline{X}$		699
P-A-F-4-S		93.0
-5	-100	95.0
-6		92.0
$\overline{X}$		93.3
P-A-F-7-S		64.1
-8	75	63.1
-12		62.3
$\overline{X}$		63.2
P-A-F-9-S		40.3
-10	350	42.4
-11		43.8
$\overline{X}$		42.2
P-A-F-21-S		22.2
-22	600	24.4
-23		23.7
$\overline{X}$		23.4

NOTE: All specimens failed 100% cohesive in ESM

FIGURE 13

ESM 1004 AP VACUUM STRIPPED MATERIAL
RECESSION DATA